Crude to olefins: effect of feedstock composition on coke formation in a bench-scale steam cracking furnace

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Supporting information

S1 Effluent analysis details

In the following three paragraphs, a detailed description of the two gas chromatographs for effluent analysis, i.e., GC×GC and RGA, is given.

S1.1 GC×GC

Reactor effluent is sampled on-line, i.e., during the experiment, at high temperature using a PLC controlled valve-based sampling system [1]. Condensation of heavy reaction products is avoided by keeping the valve system at a temperature of 573 K in the so-called sample box. A sample taken in the gas phase is directed to the Thermo Fisher Scientific Inc. (Waltham, USA) Trace 1310 GC × GC set-up (supplied by Interscience, Belgium) via a Split/Splitless injector kept at 593 K with a split flow of 100 ml min^{-1}. PONA column (SGE Analytical Science, 50 m, 0.15 mm, 0.5 µm) is used as a first dimension column, while a BPX-50 (SGE Analytical Science, 7.5 m, 0.25 mm, 0.25 µm) is used as the second dimension column. Modulation is performed using a reversed-flow differential flow modulator [2] with a sample loop volume of 25 µl (SepSolve Analytics, United Kingdom). The modulation time is set to 2 s, with a flush time of 110 ms. A bare silica bleed line (7.7 m, 0.10 mm) is connected to another FID which serves as a check in case of a bleed of hydrocarbons from the sample loop during the refill stage. The initial temperature of the chromatographic oven is kept for 4 min at 233 K by injection of liquid nitrogen, before being increased to a temperature of 313 K with a heating rate of 4 K min^{-1}. Subsequently, the temperature is increased to 573 K with a heating rate of 5 K min^{-1}. Helium carrier gas flow of 0.5 ml min^{-1} is used for the first dimension column, while 20 ml min^{-1} is used for the second dimension column. The scan frequency of both FIDs, i.e., connected to the second dimension column and to the bleed

line, is 100 Hz. Hyperchrome Data System from Thermo Fisher Scientific Inc. (Waltham, USA) is used for acquisition and processing of results. The raw GC × GC-FID data were exported to a NetCDF file and subsequently processed by GCImage™, LLC 2.6b4 software (Lincoln, Nebraska, USA).

S1.2 RGA

Downstream of the TLE and the high temperature sampling section, the effluent stream is cooled to 320 K using a water-cooled heat exchanger. Water and heavy hydrocarbon products, i.e., a fraction of Pyrolysis Gasoline (Pygas) and Pyrolysis Fuel Oil (PFO), are condensed and collected in a knock-out drum. Uncondensed lighter reaction products are sampled on-line and directed to the so-called refinery gas analyser RGA (Interscience, Belgium) before sending the stream to the vent line. The RGA is equipped with three detectors working on parallel channels, i.e., two TCDs and an FID. The TCD detectors allow detection of N_2, CO, CO_2, H_2, and the later hydrocarbons and hydrocarbons up to two carbon atoms, while the FID allows the detection of hydrocarbons up to four carbon atoms. Each detector is connected to a different chromatographic column. The RGA settings are presented in table A1.

RGA			
Detector	FID	TCD 1	TCD 2
Carrier gas	He	He	N_2
Pre-column	Fused Silica Capillary Precolumn (5 m × 0.53 mm × 3 μm)	Packed Porous Polymers Column (0.25 m × 1.6 mm)	Packed Porous Polymers Column (1 m × 1.6 mm)
Analytical column(s)	Alumina bond PLOT Column	Packed Porous Polymers Column	Carbon Molecular Sieve Column

	(25 m × 0.53 mm × 10 μm)	(1 m × 1.6 mm) Molecular Sieve Column (2 m × 1.6 mm)	(3 m × 1.6 mm)
Oven temperature	333 (2 min) → 473 K (1.3 min) (30 K min^{-1})	353 K	353 K
Detector Temperature	523 K	383 K	383 K

Table S1: RGA settings for on-line effluent measurements

Elemental Analysis			**ASTM-D2887 (K)**		
	NF	WRGO		NF	WRGO
Carbon (wt.%)	85.4 ± 0.07	84.89 ± 0.15	0%	305	321
Hydrogen (wt.%)	14.6 ± 0.09	13.99 ± 0.09	5%	316	373
Nitrogen (wt.%)	<0.01a	0.06 ± 0.01	10%	323	410
Sulfur (wt.%)	<0.01a	1.07 ± 0.07	20%	343	442
Oxygen (wt.%)	<0.01a	<0.01a	30%	366	480
H/C (mol/mol)	2.06 ± 0.02	1.98 ± 0.02	40%	380	516
GC × GC			50%	396	551
Paraffins (wt.%)	32.8 ± 1.3	25.4 ± 1.1	60%	409	588
Isoparaffins (wt.%)	37.0 ± 1.1	36.1 ± 2.2	70%	423	622
Cycloalkanes (wt.%)	17.8 ± 0.4	7.0 ± 0.4	80%	433	663
Aromatics (wt.%)	12.4 ± 0.4	28.6 ± 1.9	90%	447	710
Bio-markers (wt.%)	<0.01[a]	2.9 ± 0.7	95%	452	740
Carbon number	5-12	5-45	100%	489	821

a) Below detection limit of the method

Table S2: Feedstock analysis for naphtha fraction (NF) and wide-range gas oil (WRGO)

Compound name	NF	WRGO
Hydrogen	0.7	0.4
Methane	8.8	9.6
Ethane	2.8	5.1
Ethylene	21.9	16.2
Propane	0.4	1.1
Propylene	14.1	12.1
Acetylene	0.2	0.2
Propadiene	0.1	0.1
Isobutane	0.2	0.1
N-butane	0.8	0.2
Trans-2-butene	0.6	0.5
N-butene	3.1	1.5
Isobutene	2.0	1.7
Cis-2-butene	0.4	0.4
Methylacetylene	0.6	0.2
1,3-Butadiene	5.1	3.3
Benzene (B)	2.7	3.4
Toluene (T)	2.9	2.3
M- & p-Xylene (X)	1.1	0.9
O-xylene	0.6	0.8
Pygas excl BTX	19.6	24.8
Pyrolysis fuel oil	11.3	14.1

Table S3: Effluent composition during naphtha fraction (NF) and wide-range gas oil (WRGO) experiment

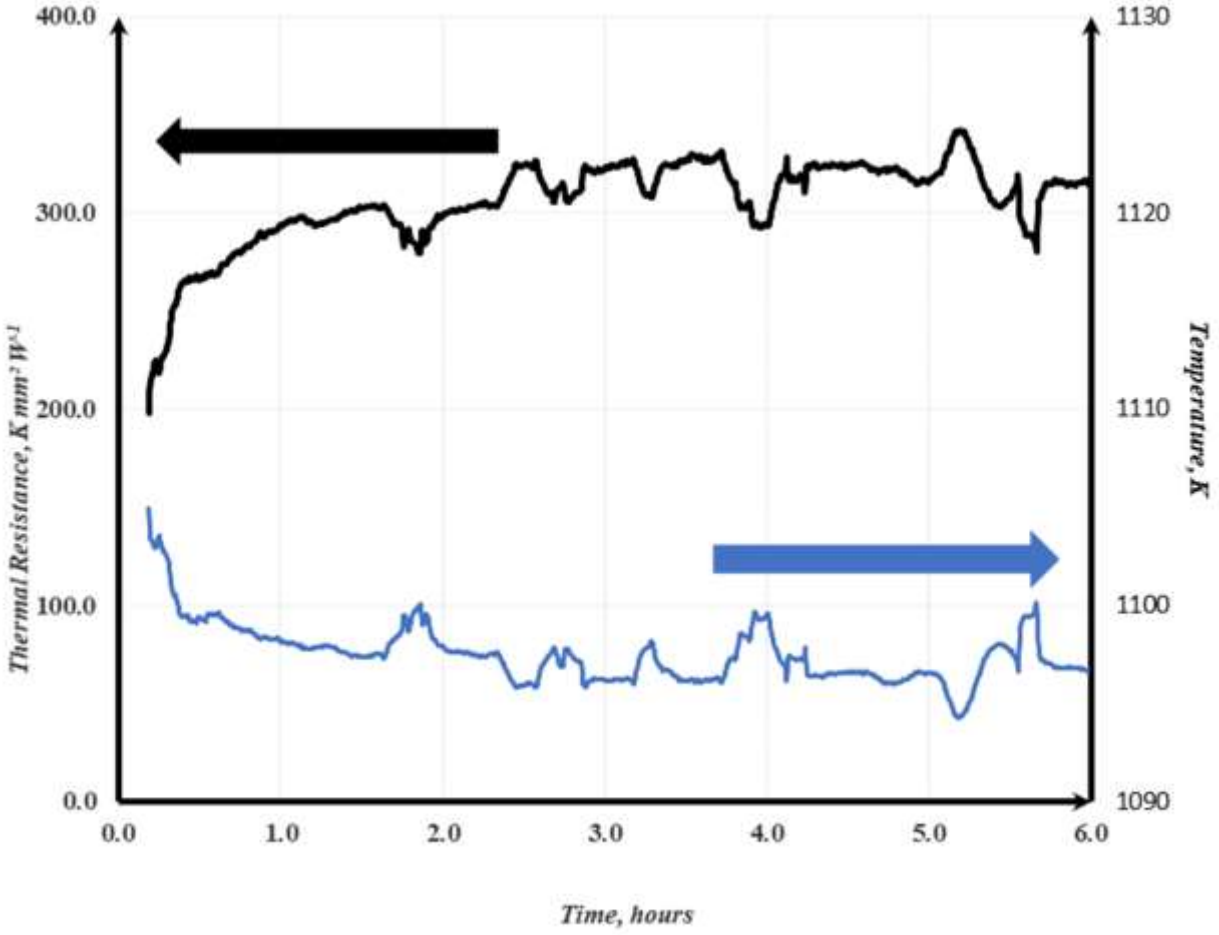

Figure S1: Reaction temperature and thermal resistance as a function of run time during a NF experiment with the movable thermocouple in radiant section zone III. Black (left axis) and blue (right axis) curves correspond to thermal resistance and process gas temperature in zone III, respectively .

References

(1) Ristic, N. D.; Djokic, M. R.; Van Geem, K. M.; Marin, G. B. On-line Analysis of Nitrogen Containing Compounds in Complex Hydrocarbon Matrixes. *Jove-Journal of Visualized Experiments* **2016**, DOI:10.3791/54236 10.3791/54236(114).

(2) Griffith, J. F.; Winniford, W. L.; Sun, K. F.; Edam, R.; Luong, J. C. A reversed-flow differential flow modulator for comprehensive two-dimensional gas chromatography. *Journal of Chromatography A* **2012,** *1226*, 116.